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Hydrothermal modification of the alumina catalyst for the skeletal isomerization of n-butenes

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ABSTRACT

Hydrothermal modification of the alumina catalyst of n-butenes skeletal isomerization was investigated. It is shown that during the hydrothermal treatment of γ-Al_2O_3 and subsequent calcination its activity in skeletal isomerization of n-butenes first increases, and then it decreases with a rise of the hydrothermal treatment duration. This behavior is due to a similar change in the content of the strong Lewis acid sites of alumina, which are the active centers of reaction and they can be identified by IR-spectroscopy of the adsorbed pyridine and EPR-spectroscopy of the adsorbed anthraquinone. We report the mechanism of new Lewis acid sites formation at the γ-Al_2O_3 hydrothermal treatment containing X-ray amorphous component.

1. Introduction

Active aluminum oxide (γ-Al_2O_3) is most often used in a series of oxide catalysts and catalyst carriers due to a unique combination of thermal stability, mechanical strength, developed surface and acid-base properties. Its acid properties affect the dispersity of the active component in the catalyst; the acid sites are the active centers in dehydration and isomerization reactions; they are also involved in oligomerization of hydrocarbons [1–10].

The skeletal isomerization of n-butenes (1-butene, trans-2-butene, cis-2-butene) to 2-methylpropene proceeds on the Lewis acid sites of γ-Al_2O_3 by the carbon-ion mechanism, including the stages of n-butene adsorption with formation of carbonium ion of linear structure, its isomerization to the tertiary ion, and desorption of 2-methylpropene [11]. Therefore, γ-Al_2O_3 with a high content of strong Lewis acid sites is used as an industrial catalyst for the skeletal isomerization of n-butenes to 2-methylpropene [12], and it is important to increase its activity [11,12]. For this purpose, chemical modification of γ-Al_2O_3 with oxides by tungsten and boron was carried out [13–16]. However, with an increase in the acidity and conversion of n-butenes, the selectivity to 2-methylpropene is reduced and catalyst surface coking occurs [14]. This is associated with a change in the structure and strength of acid sites during chemical modification. The problem can be solved by increasing the concentration of acid centers γ-Al_2O_3 without using promoters.

Several researches [2] developed a number of methods for controlling the acid properties of the γ-Al_2O_3 surface through the chemical modification and heat treatment, and showed the mechanism of their action. Another new method of acid properties modifying of surface alumina is hydrothermal treatment (HTT) with the calcination to follow: the γ-Al_2O_3 hydration into boehmite proceeds in the hydrothermal conditions, and it is then converted back to oxide with improved catalytic characteristics in results of heating [4–6]. For example, we showed the positive effect of HTT support on the catalytic properties of synthesized alumoplatinum catalysts in the dehydrogenation of propane [4] and of NiMo/γ-Al_2O_3 in the hydrogenation of quinoline [9].

Unfortunately, at the present time in the literature there is no unambiguous opinion on the process of changing the acidity of the alumina support as a product of the γ-Al_2O_3 HTT. In [4–6,9], an increase in the content of Lewis acid sites after HTT is shown. However, the causes and mechanism of acidity growth were not revealed - the authors attribute the results to the formation of a large boehmite, the particles of which have the form of plates [6]. This assumption contradicts the data of [10,11], according to which the boehmite is better crystallized, and the lower is the acidity of γ-Al_2O_3 obtained from it. On the other hand, HTT removes microimpurities of Na, Fe oxides from the alumina. This can also be the reason for the increase in the content of acid sites and their strength [2]. It is probable that hydrothermal modification can increase the acidity of γ-Al_2O_3 by changing its microstructure and/or as a result of the effect of purification from metal oxides.

The purpose of this research work is investigation of the effect of hydrothermal treatment γ-Al_2O_3 on its acid properties and catalytic

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